

Quenching of Residual Fields by Nonaxially Symmetric Dipolar Coupling in Zero-Field NMR

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Theoretical predictions and experimental results showing the quenching of residual field effects in zero-field NMR experiments are presented. The case studied is analogous to that of a spin $I = 1$ nucleus but consists of two dipolar-coupled spin $I = \frac{1}{2}$ nuclei with a nonaxially symmetric dipolar coupling. © 1987 Academic Press, Inc.

INTRODUCTION

This work was motivated by the observation that in recent zero-field NMR experiments, the spectra due to axially symmetric homonuclear dipolar couplings were broadened by residual fields, whereas those due to nonaxially symmetric couplings were not. It is well known that dipolar couplings involving integer spins can be quenched (*1*). This quenching effect has been seen to increase with the increasing asymmetry of the quadrupolar interaction and is reduced in the presence of a magnetic (local dipolar or applied) field (*1, 2*). The study of NQR lineshapes in the presence of a modulating field has long been of interest as a means of assigning NQR transitions and for determining asymmetry parameters (*3, 4*). Additionally, analytic expressions for the Zeeman effect on the energy levels of a spin $I = 1$ nucleus have also been reported (*3*). In this paper, we will discuss an analogous case of the quenching effect of residual fields with the onset of the asymmetry in the homonuclear dipolar coupling between two spin $I = \frac{1}{2}$ nuclei (a pseudo spin $I = 1$ case) in zero-field NMR.

ZERO-FIELD NMR

The theory (*5*) and experimental implementation (*6*) of time-domain zero-field NMR methods have been described in detail elsewhere and only a brief discussion will follow here. The experiment begins with polarizing a sample in a large magnetic field to produce a magnetization, M_z , where z refers to the field direction. The sample is then adiabatically demagnetized, thus maintaining its polarization, to an intermediate field, B_i . Sudden removal of B_i leaves the sample in zero field in a nonequilibrium state and evolution under the zero-field Hamiltonian occurs for a time t_1 . Reapplication of the field terminates the zero-field evolution and allows for detection of the signal

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in high field. The evolving magnetization is measured as a function of incremented intervals of t_1 to produce the zero-field interferogram.

In zero field with no preferred direction in space, the Hamiltonian is best described in a molecule fixed frame. Generally the dipolar Hamiltonian is treated as axially symmetric ($\eta = 0$) in the principal axis system of the interaction. However, through motional or symmetry effects, the resulting Hamiltonian in a molecule fixed frame may become nonaxially symmetric ($\eta \neq 0$) (7, 8). With this in mind, the zero-field dipolar Hamiltonian for two dipolar-coupled spin $I = \frac{1}{2}$ nuclei, with the z axis chosen to be along the internuclear vector, can be written

$$\mathcal{H}_D = -\frac{\gamma^2 h}{2\pi r^3} [3I_{z1}I_{z2} - \mathbf{I}_1 \cdot \mathbf{I}_2 + \eta(I_{1x}I_{2x} - I_{1y}I_{2y})]. \quad [1]$$

The Hamiltonian has no angular dependence in the laboratory frame and is identical for every crystallite in a powder sample. The energies for the triplet manifold of two homonuclear dipolar-coupled spin $I = \frac{1}{2}$ nuclei are

$$\left. \begin{aligned} E_1 = E_2 = \frac{-\omega_D}{2} \\ E_3 = \omega_D \end{aligned} \right\} \eta = 0,$$

$$\left. \begin{aligned} E_1 = \frac{-\omega_D}{2}(1 + \eta) \\ E_2 = \frac{-\omega_D}{2}(1 - \eta) \\ E_3 = \omega_D \end{aligned} \right\} \eta \neq 0, \quad [2]$$

where $\omega_D = \gamma^2 h / 2\pi r^3$. The eigenstates and energy levels for this system, written in the zero-field basis set (5), are illustrated in Fig. 1. The additional η -dependent term is seen to lift the degeneracy of two of the levels when $\eta \neq 0$. The homonuclear dipolar-coupled system is entirely analogous to the quadrupolar spin $I = 1$ case. The similarity has been noticed for the $S = 1$ EPR case where expressions for the lineshapes in the presence of a spin-spin coupling and a field have been calculated (9). Due to this similarity, the effects of coupling to a local dipolar field (a nonresonant $I = \frac{1}{2}$ spin) or a residual field (due to incomplete cancellation in the zero-field region) should be similar to that found previously for quadrupolar spins (I), an effect which will prove useful in high-resolution zero-field NMR.

Perturbation by residual fields. We first make a rough estimate of the effect of a small residual dc field on the dipolar Hamiltonian by perturbation theory. These calculations have been presented before for $\eta \neq 0$ (10) and are repeated here for comparison to the $\eta = 0$ case. The magnitude of Zeeman interactions with the residual field, B_{res} , is assumed to be much smaller than the dipolar interaction. The zero-field Hamiltonian now contains an extra term

$$\mathcal{H}_{\text{ZF}} = -\frac{\gamma^2 h}{2\pi r^3} [3I_{z1}I_{z2} - \mathbf{I}_1 \cdot \mathbf{I}_2 + \eta(I_{x1}I_{x2} - I_{y1}I_{y2})] + \gamma B_{\text{res}} [\sin \theta \cos \phi (I_{x1} + I_{x2}) \\ + \sin \theta \sin \phi (I_{y1} + I_{y2}) + \cos \theta (I_{z1} + I_{z2})]. \quad [3]$$

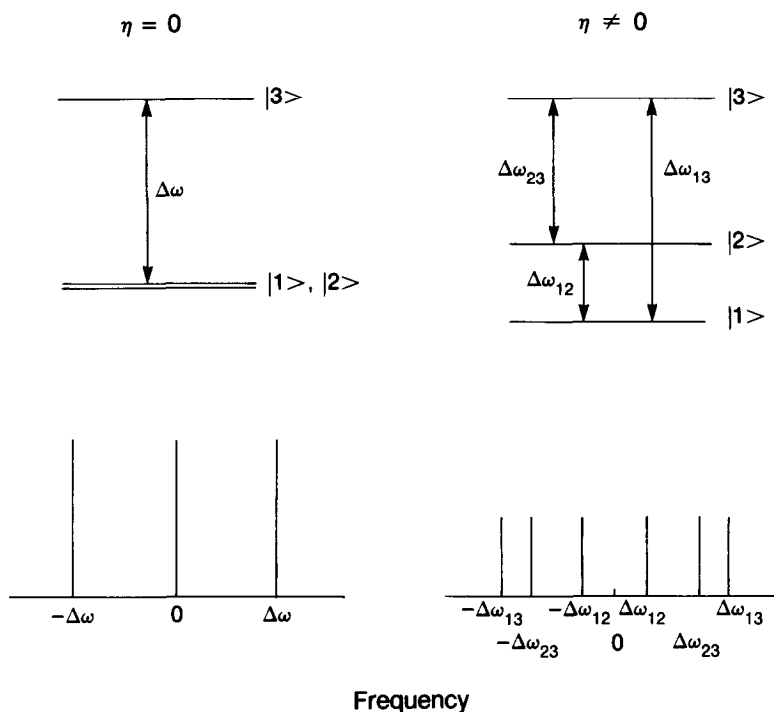


FIG. 1. Unperturbed triplet manifold energy levels, eigenstates, and predicted spectral transitions of the zero-field homonuclear dipolar Hamiltonian (Eq. [1] in the text) with $\eta = 0$ and $\eta \neq 0$. The eigenstates are written in terms of the zero-field basis set for two homonuclear spin $I = \frac{1}{2}$ nuclei and for both cases are given as $|1\rangle = 2^{-1/2}(|\alpha\alpha\rangle + |\beta\beta\rangle)$, $|2\rangle = -i2^{-1/2}(|\alpha\alpha\rangle - |\beta\beta\rangle)$, and $|3\rangle = 2^{-1/2}(|\alpha\beta\rangle + |\beta\alpha\rangle)$. The zero-field energy levels are independent of orientation as can be seen from their respective energies E_1 , E_2 , and E_3 in Eq. [2] in the text. The η term of the Hamiltonian lifts the degeneracy of the two lowest energy levels. The lines which appear in the zero-field spectrum are of equal intensity in the absence of a perturbation. The zero-frequency line in the $\eta = 0$ cases arises from nonevolving magnetization corresponding to the degenerate energy levels.

The angular terms relate the residual field, assumed to be in the lab z direction, to the molecular frame. If $\eta \neq 0$, one can easily show that the perturbation does nothing to first order as the matrix elements of I_x , I_y , and I_z are zero ($l, 2$). To second order in the perturbation the resulting energy levels for $\eta \neq 0$ are

$$\begin{aligned}
 E_1 &= -\frac{\omega_D}{2}(1 + \eta) - \frac{D_z^2}{\omega_D \eta} - \frac{2D_x^2}{\omega_D(3 + \eta)} \\
 E_2 &= -\frac{\omega_D}{2}(1 - \eta) + \frac{D_z^2}{\omega_D \eta} - \frac{2D_y^2}{\omega_D(3 - \eta)} \\
 E_3 &= \omega_D + \frac{2D_y^2}{\omega_D(3 - \eta)} + \frac{2D_x^2}{\omega_D(3 + \eta)},
 \end{aligned}
 \tag{4}$$

where the D terms contain the orientation dependence of the residual field in the molecular frame: $D_x = \gamma B_{\text{res}} \sin \theta \cos \phi$, $D_y = \gamma B_{\text{res}} \sin \theta \sin \phi$, and $D_z = \gamma B_{\text{res}} \cos \theta$. The perturbation is seen to shift the energy levels quadratically in second order and the low frequency transition ($E_1 - E_2$) is affected most strongly. The shift in energy levels is different for each crystallite orientation due to the angular dependence in the D terms and results in a linebroadening effect when averaged over all orientations. From these expressions, it is evident that as η increases the shift in energy levels decreases.

When $\eta = 0$, due to the degeneracy of two of the zero-field energy levels, degenerate perturbation theory must be used to describe the situation. In this case, the degeneracy is lifted to first order linearly in the residual field. To second order the resulting energy levels for $\eta = 0$ are

$$\begin{aligned} E_1 &= -\frac{\omega_D}{2} - D_z - \frac{1/2(D_x^2 + D_y^2)}{3\omega_D/2 + D_z} \\ E_2 &= -\frac{\omega_D}{2} + D_z - \frac{1/2(D_x^2 + D_y^2)}{3\omega_D/2 - D_z} \\ E_3 &= \omega_D + \frac{1/2(D_x^2 + D_y^2)}{3\omega_D/2 + D_z} + \frac{1/2(D_x^2 + D_y^2)}{3\omega_D/2 - D_z}. \end{aligned} \quad [5]$$

The effective perturbation is larger for $\eta = 0$ as it is a first-order effect. The spectrum in either case will involve a distribution of Eqs. [4] or [5] over all relative orientations of B_{res} .

Numerical simulations. The effect of the residual fields can be illustrated through numerical simulations. The residual field is chosen to be along the laboratory z axis as this is generally the largest component present in practice (6). Of course the actual direction of the residual field has no effect on the form of the zero-field Hamiltonian. The simulations calculate the shift in energy levels for each relative orientation of the field direction in the molecular frame. The normalized signal, $S(t_1)$, is then calculated as a sum over all orientations from

$$S(t_1) = \text{Tr}\{R I_z R^{-1} \exp(-i\mathcal{H}_{\text{ZF}} t_1) R I_z R^{-1} \exp(i\mathcal{H}_{\text{ZF}} t_1)\}, \quad [6]$$

where $R = \exp(-i\phi I_z) \exp(-i\theta I_y)$ is the transformation between the lab and zero-field frames. The appearance of the spectrum depends most strongly on the relative orientations of the initial condition and the residual field and, of course, the relative magnitudes of the zero-field interaction and the residual field.

The simulated spectra for a given residual field and increasing η values appear in Fig. 2. For $\eta = 0$, the linebroadening of the high-frequency line is significantly greater than for an individual line with $\eta \neq 0$. The low-frequency peak is most strongly affected as predicted from the perturbation theory calculations and the component at zero frequency results from the fact that the residual field and initial magnetization are collinear; thus a component remains along the z axis and does not evolve. As expected this peak increases in size with increasing levels of the residual field. In the limit of a residual z field which is greater than the local interactions, a large proportion of the magnetization will remain locked along the field direction although interest-

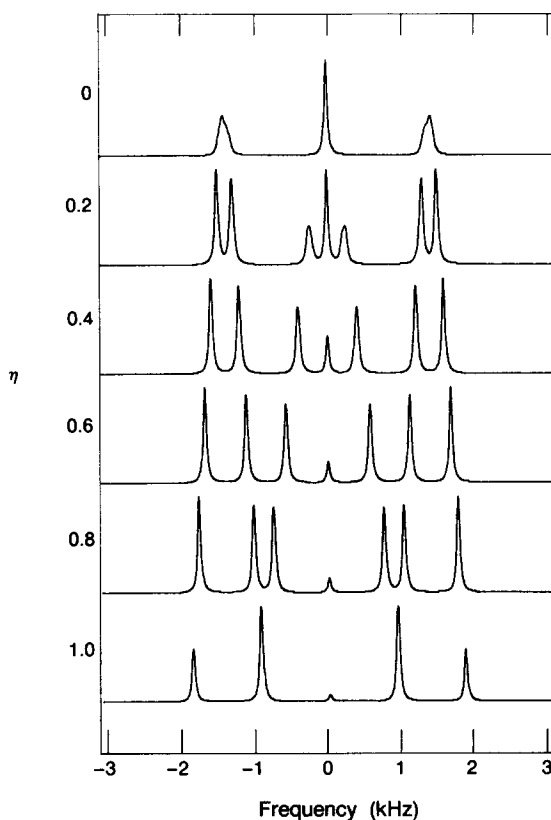


FIG. 2. Numerical simulations of zero-field NMR spectra of two dipolar coupled spin $I = \frac{1}{2}$ nuclei with a residual field of 0.025 G in the laboratory z direction and increasing values of η . The first spectrum with $\eta = 0$ shows substantial broadening of the high-frequency lines. The zero-frequency peak corresponds to nonevolving magnetization proportional to $I_{z,\text{lab}}$ and is not strongly affected by the field. With a nonzero value of η , the low-frequency lines are most affected by the residual field showing broadening and a decrease in intensity. In addition, a peak appears at zero frequency which should not occur when $\eta \neq 0$. This peak is a component of the magnetization which does not evolve but rather remains along the residual field. The effect of the residual field decreases noticeably as individual lines broaden very little (although are altered in intensity) with larger values of η . (Note that the spectra are not plotted to scale as the integrated intensity is in fact constant.)

ing low-field NMR phenomena result with the sudden transition in intermediate field (11).

EXPERIMENTAL RESULTS

The quenching effect has been experimentally observed in two liquid crystal systems. The zero-field NMR spectra of these systems have been described previously (8). Briefly, the samples consist of a CH_2Cl_2 probe molecule in mixtures of differing proportions of two liquid crystals to produce smectic B and smectic E phases (12). Both are ordered powder-like phases, the former with axial symmetry and the latter a biaxial phase (13) thereby inducing an asymmetry in the homonuclear dipolar coupling tensor.

The spectra display inherently narrow lines due to the lack of intermolecular dipolar couplings. Typically a residual field of approximately 0.025 G results from shimming the zero-field region with a gaussmeter. The liquid crystal samples, with very small dipolar frequencies ($\omega_D \approx 1$ kHz) and narrow lines, have made it necessary to improve upon this. The zero-field NMR spectra taken under identical experimental conditions are compared with computer simulations in Fig. 3. The spectrum of the axially symmetric dipolar interaction shows the effect of a residual field in the broadening of the outer lines and narrow zero-frequency peak. In the case of a nonzero η in the biaxial phase, the effect of the residual field is reduced although the decreased intensity of the low-frequency lines and the peak at zero frequency are clear evidence of its presence.

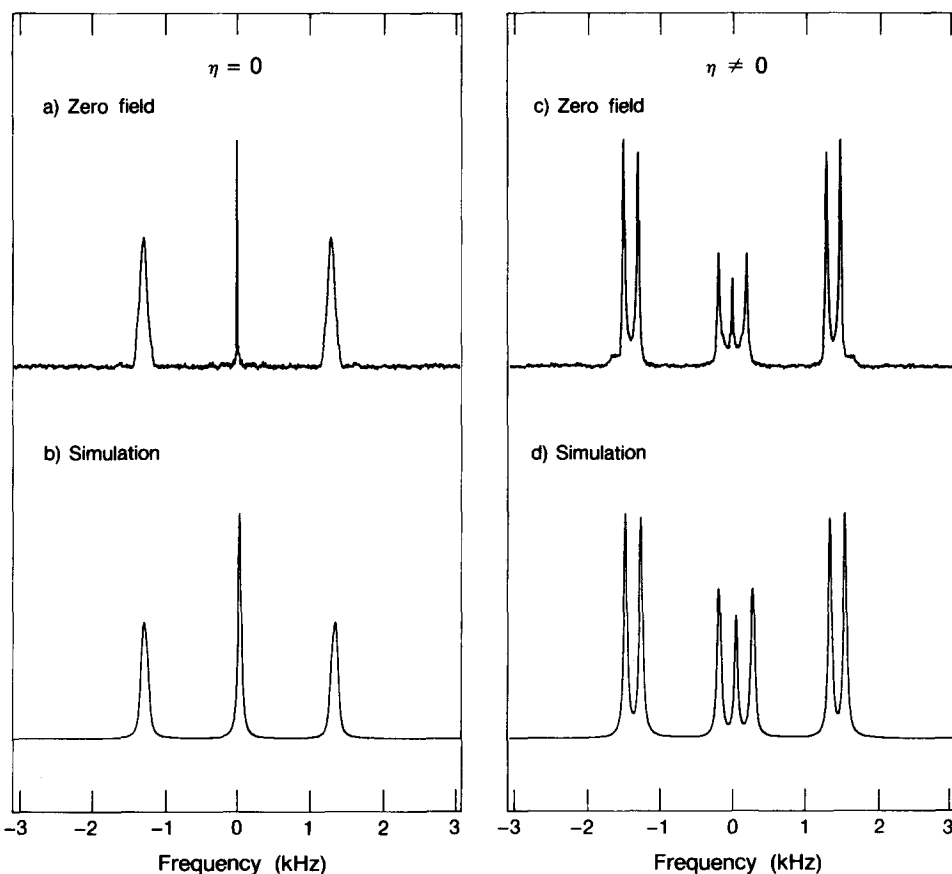


FIG. 3. Experimental spectra of CH_2Cl_2 in smectic B (axially symmetric, $\eta = 0$) and E (nonaxially symmetric, $\eta \neq 0$) phases and computer simulations of the effect of a residual field. For $\eta = 0$, the high-frequency lines in (a) are broadened considerably relative to the line at zero frequency. The simulation in (b) was produced with a residual z field of 0.0175 G and is broadened slightly with a Lorentzian function. In (c) the linewidths with $\eta \neq 0$ are quite narrower than those in the former case. The simulation shown in (d) uses the same residual field as (b) and shows the expected broadening of the low-frequency lines, the altered intensities, and the zero-frequency peak.

The effects of residual fields can be removed from the zero-field spectrum by using a dc pulsed field as a refocusing echo pulse in analogy to a high-field Hahn echo (14). For samples such as aligned nematic liquid crystals, a 180° pulse applied in the middle of the zero-field t_1 interval will refocus the magnetization and remove the line broadening (15). For powder samples, the normalized signal after a dc pulse in the laboratory x direction can be calculated from

$$S(t_1) = \text{Tr}\{RI_zR^{-1}\exp(-i\mathcal{H}_D t_1/2)R\exp(-i\pi I_x)R^{-1} \\ \times \exp(-i\mathcal{H}_D t_1/2)RI_zR^{-1}\exp(i\mathcal{H}_D t_1/2)R\exp(i\pi I_x)R^{-1}\exp(i\mathcal{H}_D t_1/2)\}, \quad [7]$$

which for the normalized signal averaged over all molecular orientations is

$$S(t_1) = 1/15(5 + 4 \cos 3/2(S\omega_D t_1/2) + 6 \cos 3/2(S\omega_D t_1)), \quad [8]$$

where S is the liquid crystalline order parameter which scales the dipolar interaction (16). The analytic expression shows that not all the signal is refocused and will show no effect of the residual field. A certain component evolves for only half the t_1 period and is then broadened by the residual field to half the width of the original line. The experimental spectrum of the smectic B phase with a 180° dc pulse is shown in Fig. 4. The high-frequency lines are narrowed appreciably and the half-frequency broad lines are evident.

CONCLUSIONS

The residual field quenching by homonuclear dipolar-coupled spin $I = \frac{1}{2}$ nuclei has been shown experimentally and is in agreement with predictions made from perturbation theory and numerical simulations. This effect is analogous to that seen for integer spin systems in NQR experiments (1). The simulations assume a residual field

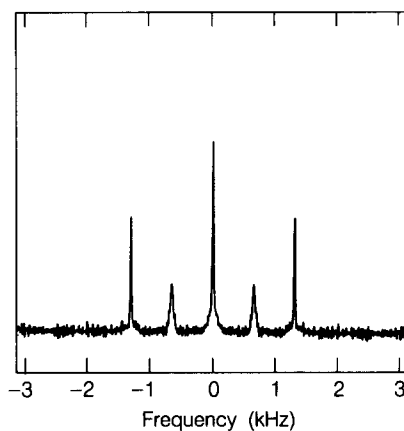


FIG. 4. Experimental spectrum of CH_2Cl_2 in smectic B phase after the application of a dc refocusing π pulse in the laboratory x direction in the middle of the zero-field period. The signal appears as predicted by Eqs. [7] and [8] in the text with a portion of the magnetization refocused into narrow lines at the higher dipolar frequencies. At half this frequency, magnetization which evolves under the residual field for only one-half the zero-field period produces a broadened line.

in the laboratory z direction but can easily incorporate any field direction. As stated above, altering the direction of the residual field will not affect the zero-field Hamiltonian when averaged over a powder distribution, but altering the relative orientations of the initial condition and residual field will affect the appearance of the spectrum (7). Through pulsed dc field experiments which remove the effects of very small residual fields, high-resolution spectra of disordered materials are obtained.

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